

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08L 65/00, 77/00	A1	(11) International Publication Number: WO 93/06171 (43) International Publication Date: 1 April 1993 (01.04.93)
(21) International Application Number: PCT/US92/07953 (22) International Filing Date: 22 September 1992 (22.09.92) (30) Priority data: 765,292 25 September 1991 (25.09.91) US (71) Applicant: MONSANTO COMPANY [US/US]; 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US). (72) Inventors: ASRAR, Jawed ; 14949 Royal Brook, Chesterfield, MO 63017 (US). GOMAN, Peter, Malcom ; 11 Dixon Street, Tarrytown, NY 10591 (US). (74) Agent: BOLDING, James, Clifton; Monsanto Company, 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).		(81) Designated States: CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE). Published <i>With international search report.</i>
(54) Title: POLYMER BLENDS OF NORBORNENE DICARBOXIMIDES (57) Abstract Polymer blends comprising (a) a metathesis ring-opening polymerized unsaturated polymer of norbornene dicarboximide monomer units and/or a metathesis ring-opened unsaturated copolymer of norbornene dicarboximide and a norbornene carboxylic acid monomer units and (b) a polymer having acid-reactive functionality, e.g. a polyamide such as nylon-6 or nylon-6,6. The norbornene dicarboximide monomers can be alkyl, cycloalkyl or aromatic imide, preferably methyl, ethyl, propyl, isopropyl, cyclohexyl or phenyl imides. Preferred norbornene carboxylic acid monomer units are norbornene dicarboxylic acids, acid anhydrides, monoesters or diesters.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	MN	Mongolia
AU	Australia	FR	France	MR	Mauritania
BB	Barbados	GA	Gabon	MW	Malawi
BE	Belgium	GB	United Kingdom	NL	Netherlands
BF	Burkina Faso	GN	Guinea	NO	Norway
BG	Bulgaria	GR	Greece	NZ	New Zealand
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	PT	Portugal
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	RU	Russian Federation
CG	Congo	KP	Democratic People's Republic of Korea	SD	Sudan
CH	Switzerland	KR	Republic of Korea	SE	Sweden
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovak Republic
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CS	Czechoslovakia	LU	Luxembourg	SU	Soviet Union
CZ	Czech Republic	MC	Monaco	TD	Chad
DE	Germany	MG	Madagascar	TG	Togo
DK	Denmark	ML	Mali	UA	Ukraine
ES	Spain			US	United States of America

POLYMER BLENDS OF NORBORNENE DICARBOXIMIDES

Disclosed herein are metathesis ring-opened unsaturated polymers of norbornene dicarboximides and copolymers of norbornene dicarboximide and norbornene dicarboxylic acid, anhydride, mono ester or diester. Also disclosed are blends of such polymers and copolymers with polymers having acid-reactive functionality, e.g. a polyamide such as nylon-6 or nylon-6,6 and, optionally, a rubber toughening agent. Also disclosed are methods of using such blends for high performance thermoplastic applications.

BACKGROUND OF THE INVENTION

Polyamides, e.g. nylon-6 and nylon-6,6, are typically characterized as semicrystalline thermoplastics and are widely used in a wide range of applications. Due to high strength polyamides are commonly and advantageously used as tire cord, carpet fiber, tough fabrics, etc. However, due to other properties polyamides have limited use in other engineering thermoplastic applications. For instance, due to low impact strength, polyamides often require toughening, e.g. with rubber impact modifier, to provide sufficient impact strength required of many molded parts. Polyamides also typically have unsatisfactory load bearing properties at moderate to high temperatures due to the low glass transition temperature of the polyamide. Heat distortion temperature determined under the force of a load (typically 1820 Kpa) is widely known by the acronym "HDTUL". For instance, nylon-6 and nylon-6,6 have HDTUL in the range of 60 to 80 °C. Rubber-modified polyamides, having high impact strengths that commend their use for many engineering thermoplastic applications, generally have even lower HDTUL. Metathesis ring-opening polymers of norbornene dicarboximides, especially the N-methyl,

-2-

N-ethyl, N-propyl and N-phenyl imides, exhibit high glass transition temperatures, e.g. about 200 °C, and high HDTUL, e.g. about 150 to 180 °C. What I have discovered is that such metathesis ring-opening
5 polymers of norbornene dicarboximides can be effectively blended with polyamides to provide blends having the attendant advantageous properties of polyamides but with an exceptionally high heat
10 distortion temperature. Even more advantageous blends are achieved when the metathesis ring-opened unsaturated polymer of norbornene dicarboximide includes a small amount of an acid containing species.

SUMMARY OF THE INVENTION

In one aspect this invention provides
15 polymer blends comprising a metathesis ring-opening polymerized unsaturated polymer of norbornene dicarboximide and a polyamide or other polymer having acid-reactive functionality. In another aspect this invention provides polymer blends comprising a
20 metathesis ring-opening polymerized unsaturated copolymer of monomer units of norbornene dicarboximide and a norbornene carboxylic acid. Such copolymer can be used alone in blends with acid-reactive polymers or, alternatively, as a compatibilizer in blends of
25 norbornene dicarboximide polymer and acid-reactive polymers.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The polymer blends of this invention comprise polymers having acid-reactive functionality
30 such as polyamides and metathesis ring-opening polymerized unsaturated polymers of a norbornene dicarboximide, e.g. about 10 to 90 parts by weight of polymer having acid-reactive functionality and, conversely, about 90 to 10 parts by weight of
35 metathesis ring-opening polymerized unsaturated polymer. More preferred blends, depending on the desired properties, can comprise at least about 30

parts by weight of each polymer. Preferred polymers having acid-reactive functionality include polyamides having amine end groups such as nylon-6 or nylon-6,6 and, optionally, toughened polyamides, e.g. having rubber toughening agents. Other useful acid-reactive functional polymers include polyesters having hydroxyl end groups.

The norbornene dicarboximide of the metathesis ring-opening polymerized polymers can be alkyl, cycloalkyl or aromatic imides. Polymers having advantageously high glass transition temperatures, e.g. above 150 °C, and preferably above 200 °C, include polymers and copolymers comprising monomer units of N-methyl, N-ethyl, N-propyl, N-isopropyl, N-cyclohexyl or N-phenyl norbornene dicarboximide. Such polymers can be prepared by known methods for metathesis ring-opening polymerization of norbornene derivative monomers which provide unsaturated polymer. Especially preferred methods are disclosed by Hardiman in WIPO International Publication Number WO 91/18938.

In preferred blends the metathesis ring-opening polymerized polymer comprises a copolymer of a norbornene derivative monomer having acid functionality that allows reactive interaction with polymers having acid-reactive functionality. Preferred metathesis ring-opening polymerized unsaturated copolymers comprise monomer units of norbornene dicarboximide and a norbornene carboxylic acid or ester. In more preferred copolymers the norbornene carboxylic acid will comprise a dicarboxylic acid or the acid anhydride, mono ester or diester thereof. Although the amount of norbornene carboxylic acid functional monomer units in the copolymer can vary, preferred copolymer will generally comprise less than about 10 mole percent of the acid monomer units, e.g. about 0.5 to 3 mole percent of

acid monomer units. Such compatibilizer copolymers can readily be prepared from mixtures of monomer using metathesis ring-opening polymerization methods generally useful for norbornene derivative monomers.

5 The acid-functional copolymers of this invention can be used by themselves in blends with polymers having acid-reactive functionality, e.g. to provide blends of copolymer and polyamide. Alternatively, the acid-functional copolymers of this
10 invention can be used as additives to compatibilize blends of norbornene dicarboximide polymer and polymers having acid-reactive functionality, e.g. blends of poly(N-methyl norbornene dicarboximide) and nylon-6. The compatibilization of such blends is
15 facilitated in that the low level of acid functionality provides reactive compatibilization with the polyamide and the structural similarity provides miscibility compatibilization with the norbornene dicarboximide polymer.

20

EXAMPLE 1

A polymer of N-methyl norbornene dicarboximide monomer units was prepared by dissolving 4.5 kilograms of N-methyl norbornene dicarboximide in 9.9 kilograms of toluene at 65 °C. After adding 38.5 ml of hexene-1, a molecular weight controlling agent, to the agitated solution, polymerization was effected by adding 114.5 ml of a catalyst solution (0.5 M tungsten hexachloride and 1.5 M diethylacetal of formaldehyde in toluene) and 214 ml of diethyl aluminum chloride. The exothermic metathesis ring-opening polymerization raised the solution temperature to 105 °C in about 20 minutes. After the temperature was reduced to 65 °C stabilizers, e.g. 200 ml of methanol solution of 46 g of an ortho di-t-butyl phenol (Irganox 3125 antioxidant from Ciba-Geigy) and 24 g of tris nonyl phenyl phosphate (Polyguard U.V. stabilizer from Uniroyal) were mixed into the

-5-

polymer. The reaction product was chopped, dried, ground and washed with methanol providing 4.4 kg of a poly(N-methyl norbornene dicarboximide) homopolymer.

The homopolymer was intimately blended with an equal parts by weight of an EPDM rubber-modified nylon-6,6 (Zytel ST-801 from DuPont) in a Braybender twin screw extruder having barrel and nozzle temperatures of about 300 °C and screw speed of 80-90 rpm. Samples for analysis were extruded through an Arburg molder at about 300 °C and 6900 kPa into molds at about 130 °C. Analytical results of the properties of each of the blend are reported in Table 1.

For characterization, the polymers and blends were injection molded into specimen bars (127 mm x 12.7 mm x 3.2 mm) which were conditioned for at least 24 hours at 23 °C and 50% relative humidity. HDTUL was measured according to ASTM D-648; tensile strength, tensile modulus and elongation were measured according to ASTM D-638; flexural strength and flexural modulus were measured according to ASTM D-790; and notched Izod impact strength was measured according to ASTM D-256.

TABLE 1

	EPDM rubber modified nylon-6,6	Polymer-1*	50/50 BLEND
HDTUL (°C)	71	170	110
Tensile:			
Strength (MPa)	52	70	48
Modulus (GPa)	-	3.3	1.9
Elongation (%)	40	3	4
Flexural:			
Strength (MPa)	-	130	77
Modulus (GPa)	1.7	3.0	1.6
Notched Izod Impact			
Strength (J/M)	900	26	37

*poly(N-methyl norbornene dicarboximide)

-6-

EXAMPLE 2

A rubber modified polymer of N-methyl norbornene dicarboximide was prepared in the manner of Example 1, except that a solution of 15 g of HycarTM nitrile rubber (Goodrich) and 135 g of 1,2-dichloroethane was polymerized using 3.4 ml of the 0.5 m tungsten hexachloride catalyst solution and 5.6 ml of a 2 M solution of diethyl aluminum chloride in heptane. After the polymerization, 1.5 g of Irganox 1076 hindered phenol antioxidant (Ciba-Geigy) and 0.75 g of Polygard U.V. stabilizer (Uniroyal) were added to the polymer. The polymer was characterized and blended with an equal part of nylon-6. Properties of the polymers and blends are reported in Table 2.

TABLE 2

	<u>Nylon-6</u>	<u>Polymer-2*</u>	<u>50/50 BLEND</u>
HDTUL (°C)	58	180	110
Tensile:			
Strength (MPa)	52	63	40
Modulus (GPa)	1.9	2.2	2.6
Elongation (%)	120	10	2
Flexural:			
Strength (MPa)	97	120	70
Modulus (GPa)	2.2	2.7	2.8
Notched Izod Impact			
Strength (J/M)	58	130	21

*nitrile rubber-modified poly(N-methyl norbornene dicarboximide)

EXAMPLE 3

The polymerization of N-methyl norbornene dicarboximide was repeated essentially in the manner of Example 1 except that monomer solution contained about 2 percent norbornene dicarboxylic acid anhydride, providing an acid functionalized copoly(N-methyl norbornene dicarboximide/norbornene dicarboxylic anhydride) comprising about 1 percent monomer with acid functionality and having an inherent

-7-

viscosity of 0.47, an HDTUL of 160 °C, Flexural strength of 140 MPa and flexural modulus of 3 GPa.

Equal parts of acid anhydride-modified copolymer were blended with equal parts of each of the following polymers: (a) nylon-6,6 (Vydyne 21 from Monsanto), (b) EPDM rubber-modified nylon-6,6 (Zytel ST-801 from DuPont) and (c) a rubber-modified nylon-6 (65% nylon-6, 292 Kraton G 1652 styrene-butadiene block copolymer and 6% Kraton 1901X maleated styrene-butadiene block copolymer). The polymers were blended in the manner of Example 1 in a Braybender twin screw extruder; properties of molded samples of the 50/50 blends are reported in Table 3.

TABLE 3

50/50 Blends of Acid Anhydride-modified Copolymer with:

	<u>Nylon-6,6</u>	EPDM rubber modified <u>Nylon 6,6</u>	SB rubber modified <u>Nylon-6</u>
HDTUL (°C)	150	157	140
Tensile:			
Strength (MPa)	62	2.3	24
Modulus (GPa)	3.0	340	1.9
Elongation (%)	2.4	24	35
Flexural:			
Strength (MPa)	240	100	70
Modulus (GPa)	5.6	2.0	130
Notched Izod Impact			
Strength (J/M)	26	660	90

While specific embodiments have been described herein, it should be apparent to those skilled in the art that various modifications thereof can be made without departing from the true spirit and scope of the invention. Accordingly, it is intended that the following claims cover all such modifications within the full inventive concept.

WHAT IS CLAIMED IS:

1. A polymer blend comprising a metathesis ring-opening polymerized unsaturated polymer of norbornene dicarboximide monomer units and a polyamide.

2. A polymer blend according to claim 1 wherein said norbornene dicarboximide monomer units are alkyl, cycloalkyl or aromatic imides.

3. A polymer blend according to claim 2 wherein said norbornene dicarboximide monomer units are methyl, ethyl, propyl, isopropyl, cyclohexyl or phenyl imides.

4. A polymer blend according to claim 3 wherein said polyamide is nylon-6 or nylon-6,6.

5. A polymer blend according to claim 4 wherein said polyamide further comprises a rubber toughening agent.

6. A polymer blend according to claim 1 further comprising a metathesis ring-opening polymerized unsaturated copolymer of norbornene dicarboximide and norbornene carboxylic acid, acid anhydride, monoester or diester monomer units.

7. A polymer blend comprising (a) a metathesis ring-opening polymerized unsaturated copolymer of norbornene dicarboximide and norbornene carboxylic acid, acid anhydride, monoester or diester monomer units and (b) a polymer having acid-reactive functionality.

8. A polymer blend according to claim 7 wherein said norbornene dicarboximide monomer units are alkyl, cycloalkyl or aromatic imides.

9. A polymer blend according to claim 8 wherein said norbornene dicarboximide monomer units are an methyl, ethyl, propyl, isopropyl, cyclohexyl or phenyl imides.

10. A polymer blend according to claim 9 wherein said polymer having acid-reactive functionality is a polyamide.

11. A polymer blend according to claim 10
5 wherein said polyamide is nylon-6 or nylon-6,6.

12. A polymer blend according to claim 11 further comprising a rubber toughening agent.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/07953

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C08L65/00; C08L77/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	FR,A,2 249 913 (SHOWA DENKO) 30 May 1975 see page 28, line 11 - line 16; examples 1-31,34-36	1-12
Y	PATENT ABSTRACTS OF JAPAN vol. 1, no. 54 (C-014)25 May 1977 & JP,A,52 013 548 (SHOWA DENKO) 2 January 1977 see abstract	1-12
A	EP,A,0 409 291 (JAPAN SYNTHETIC RUBBER) 23 January 1991 see claims 1,8	1-12
<p>¹⁰ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 22 DECEMBER 1992		Date of Mailing of this International Search Report 29. 12. 92
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer KLIER E.K.

Form PCT/ISA/210 (second sheet) (January 1985)

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9207953
SA 65203**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 22/12/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-2249913	30-05-75	JP-A- 50075300	20-06-75
		DE-A, B, C 2452461	07-05-75
		GB-A- 1482993	17-08-77
		US-A- 3959234	25-05-76

EP-A-0409291	23-01-91	JP-A- 1132625	25-05-89
		JP-A- 1132626	25-05-89
		EP-A- 0317262	24-05-89
		US-A- 5053471	01-10-91

EPO FORM P0079

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

THIS PAGE BLANK (USPTO)